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Optimization of CVD Synthesis Conditions for the Synthesis of Multiwalled Carbon Nanotubes using Response Surface Methodology

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Abstract

We report the successful optimization of yield of multiwall carbon nanotube synthesized by chemical vapor deposition on Fe/Mo catalyst supported on silica using Zea mays oil as the carbon source by Chemical Vapour Deposition. The response surface methodology based on Box-Behnken design was applied to investigate the effect of parameters such as reaction Temperature, Catalytic ratio and Flow rate of carbon source. The significance of independent variables and their interactions were tested by means of the analysis of variance (ANOVA) with 95% confidence limits. High regression coefficient between the variables and the response showed of good evaluation of experimental data by polynomial regression model.

Keywords: *Box-Behnken Design; Chemical Vapour Deposition; Multiwalled Carbon Nanotubes; Zea mays oil.*

1. INTRODUCTION

Carbon nanotubes have been studied extensively since they were discovered in 1991 and have opened a new science and technology on nanoscale materials (Iijima, 1991). Carbon nanotubes have outstanding electronic, Thermal and mechanical properties because of these characteristics, a variety of potential applications such as catalyst supports, gas storage media, gas sensors, electrode materials, solar cells, flat panel displays, adsorbents, quantum wires based on the materials have been reported (Kong *et al*. 2000; Tang *et al*. 2004; Tans *et al*. 1997; Tibbetts *et al*. 2001). In general, CNTs are synthesized by arc discharge, laser ablation, CVD and spray pyrolysis methods (Ebbesen *et al*. 1992; Endo *et al*. 1995; Thess *et al*. 1996). One of the bottlenecks in the carbon nanotechnology is the growth process, which must be optimized for the achievement of worthwhile quantities of high purity material. Compared to other growth techniques of carbon nanotube, chemical vapour deposition is more suitable to satisfy the requirement of growth rate, without worsening the purity of the grown material (Kumar *et al*. 2003). In above mentioned methods methane, benzene, xylene, toluene, alcohol are mostly used as a carbon feedstock (Cui *et al*. 1999; Fab *et al*. 1999; Kong *et al*. 1998; Li *et al*. 1996; Yochi Murakami *et al*. 2003). These carbon sources are related to fossil fuels which may not be sufficient in near future. Recently, there have been appreciable attempts of carbon nanotube synthesis from regenerative precursor such as camphor, turpentine oil, pine oil, eucalyptus oil, Helianthus annuus oil (Angulakshmi *et al*. 2013; Karthikeyan *et al*. 2010; Mukul kumar *et al*. 2003; Pradip Ghosh *et al*. 2007; Rakesh *et al*. 2005).

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Response surface methodology is one such factorial design based statistical analyzing method. The experimental optimized parameters were designed on the basis of factorial design of experiments and analyzed statistically. Statistical design of experiments is the science of obtaining the largest possible amount of information about a system with the smallest number of experiments. If we take 3 levels of each parameter the maximum possible number of experiments to be performed is 27. In actual practice each and every possible combination of different levels of these parameters are difficult to investigate and evaluate. Such a screening of the experimental parameters with the theoretically lowest possible number of experiments can be done by experimental design. The experimental design develops a model, in our case regression model to study the relationship between all variable parameters and the response (Montgomery, 2000). The objective of the present paper work was to improve the yield, for the future application in nanotechnology. The major investigation of the present study includes optimization of the influencing factors on synthesis of carbon nanotubes using *Zea Mays* oil as the carbon source. The Box-Behnken plan is very convenient for a design with 3 factors and 3 variables allowing one to build a response surface model by performing 13 experiments (Myers *et al*. 1971). Some advantages of the Box-Behnken design over other response surface optimization schemes are

i) It requires the smallest number of runs for 3 factors at 3 levels,

ii) It ensures that the process remains always within the safe operation zone and

iii) it ensures that all factors are not set at their highest levels simultaneously.

Meyyappan's group has achieved considerable success in high throughput combinatorial screening of several catalysts and growth parameters for nanotube production (Cassell *et al*. 1991; Cassell *et al*. 2001; Cassell *et al*. 2003; Ng *et al*. 2003). Liu *et al*. (2012) optimize the reaction conditions for the synthesis of single walled carbon nanotubes. Nourbakhsh studied the effect of process parameters on the diameter of carbon nanotubes utilizing RSM (Amirhasan Nourbakhsh *et al*. 2007). The design was also adopted in the study to evaluate the effects of three influencing variables such as reaction temperature, catalytic ratio and flow rate of carbon source on the response of yield of carbon nanotubes.

2. EXPERIMENTAL METHODS

2.1 Carbon Nanotube Synthesis

Fe $(NO_3)_3.9H_2O$, (NH_4) Mo_7O_{24} .4 H_2O and were dissolved in methanol and mixed thoroughly with methanol suspension of silica (Merck). The solvent was then evaporated and the resultant cake heated to 90-100 °C for 3 hours, removed from the furnace and ground in an agate mortar. The fine powders were then calcined for 1 hour at 450 °C and then re-ground before loading into the reactor. The catalyst was placed on the quartz boat. The boat was placed in the heating furnace. The carrier gas nitrogen (100 ml/min) was flushed out before switch on the reaction furnace to remove air and create nitrogen atmosphere. The temperature was raised from room temperature up to the desired growing temperature. Waiting was done for 10 minutes for stabilization of temperature. Subsequently, 20 ml of *Zea mays* oil were introduced into the quartz tube through spray nozzle and the flow was maintained using saline tube at the rate of 0.5 ml/min for each precursors. The deposition time lasted for 45 minutes for each deposition at temperatures ranging from 650 °C to 850 ^{o}C. The reactor was then allowed to cool to room temperature with nitrogen gas flowing. The carbon product on the silica support was then weighed to determine the carbon yield. We define carbon yield here as the functional mass increase $(m_1\text{-}m_0) / m_0$, where m_1 and m_0 are, respectively, the final mass of the catalyst support with carbon deposit and the initial mass of the catalyst support.

The as-grown MWCNTs were purified by 40 mg of raw material was added to 20 ml 1N HCl to form an acidic slurry. This slurry was heated to 60 °C and

stirred at 600 rpm. To this heated acidic slurry 20 ml H_2O_2 was added to form oxidative slurry that continued to be heated and stirred for 30 minutes. The addition of HCl, H_2O_2, subsequent heating and stirring was repeated three more times, each time allowing the heated oxidative slurry to stir for 30 minutes. Phase separation was allowed to proceed followed by filtering the carbon phase and washing with 1N HCl and distilled water. The collected sample was dried at 120 °C in air for 2 hours. The morphology of the sample was characterized by SEM, HRTEM and Raman spectroscopic analysis.

2.1 Experimental Design

The Box-Behnken experimental design was performed with 3 factors at 3 levels (+1, 0, -1) : reaction temperature, catalyst ratio and flow rate of carbon source. The natural variables & coded variables are presented in Table 1 and 2. The effect of every process parameter on the yield of carbon nanotube was calculated by the software design expert. This software allows one to perform are necessary estimations, to determine the level of significance of all effects, to calculate the regression coefficients and to build a 3D response surface model.

Table 1. Independence Factors and their coded levels used for optimization

Variable	Real values of coded levels	
	Low	High
Temperature in degree Celsius	550	750
Flow rate of carbon source ml	10	30
Catalyst ratio in grams	0.1	1

In Table 2, a total of 17 runs were performed to optimize the process parameters and experiments were carried out according to the actual experimental design matrix. The results were analyzed applying the coefficient of determination (R^2), analysis of variance (ANOVA) and response plots. Several methods including Transmission electron microscopy, Raman spectroscopy have been suggested for assessing the quality of carbon nanotube.

Table 2. The Box-Behnken design for the three independent variables

Run	Factor 1 Temp in Deg celsius	Factor 2 Flow rate of carbon source in ml	Factor 3 Catalyst ratio in gm	Response Yield %
1	0	0	0	30
2	-1	0	-1	25
3	1	1	0	10
4	0	1	1	16
5	0	0	0	17
6	0	0	0	75
7	0	-1	-1	28
8	0	0	0	20
9	0	1	-1	15
10	-1	0	1	78
11	-1	0	1	76
12	1	-1	0	23
13	1	0	1	79
14	-1	-1	0	35
15	0	0	0	18
16	0	-1	1	21
17	1	0	-1	77

3. RESULTS & DISCUSSION

Based on our previous experience with CVD nanotube synthesis the following process variables were chosen for optimization (Colomer *et al.* 1999; Colomer *et al.* 2000; Kukovecz *et al.* 2000). A parameter set which is able to maximize the carbon nanotube yield % could be obtained analytically from eq. (1)

$$Y = 77+3.75 A+0.25B+0.75C+3AB+3.5AC+7.5BC-31.25A^2 -24.75B^2 - 27.52C^2 \quad (1)$$

Where A, B & C denote reaction temperature, catalyst ratio and flow rate of carbon source. ANOVA is a statistical technique that subdivides the total variation in a set of data into component pats associated with specific sources of variation for the purpose of testing hypotheses on the parameter of the model. The ANOVA analysis shown in Table 3 showed that temperature, catalyst ratio and flow rate of carbon source on the yield of multiwalled carbon nanotubes. The determination coefficienct ($R^2 = 0.9462$) indicates that only 1 % of the total variation is not explained by the model. The Fisher F test also demonstrates a high significance for the regression model. All of these considerations indicate a good adequacy of the regression model. The Model F- value of 186.42 implies the model is significant. There is only a 0.01% chance that a F-Value this large could occur due to noise. The data were also analyzed to check the correlation between the experimental and predicted yield (Y in %) as shown in Fig. 1. The experimental values were the measured response data for the runs designed by the Box-Behnken model, while the predicted values were obtained by calculation from the quadratic equation.

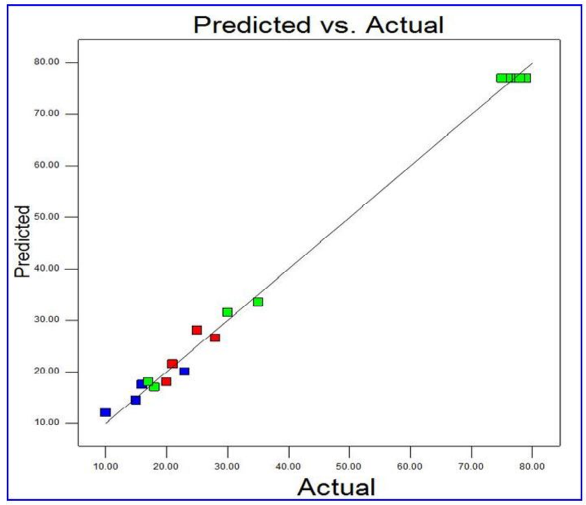

Fig. 1: Plot of the actual and predicted values

Table 3: ANOVA for response surface quadratic model

Source	Sum of Squares	df	Mean Square	F Value	p- value
Model	11384.97059	9	1264.996732	186.4206	< 0.0001
A-Temperature	112.5	1	112.5	16.57895	0.0047
B-Catalyst ratio	0.5	1	0.5	0.073684	0.7939
C-Flow rate of Carbon Source	4.5	1	4.5	0.663158	0.4423
AB	36	1	36	5.305263	0.0547
AC	49	1	49	7.221053	0.0312
BC	225	1	225	33.15789	0.0007
A^2	4111.842105	1	4111.842105	605.9557	< 0.0001
B^2	2579.210526	1	2579.210526	380.0942	< 0.0001
C^2	3126.578947	1	3126.578947	460.759	< 0.0001
Residual	47.5	7	6.785714286		
Lack of Fit	37.5	3	12.5	5	0.0770
Pure Error	10	4	2.5		
Cor Total	11432.47059	16			

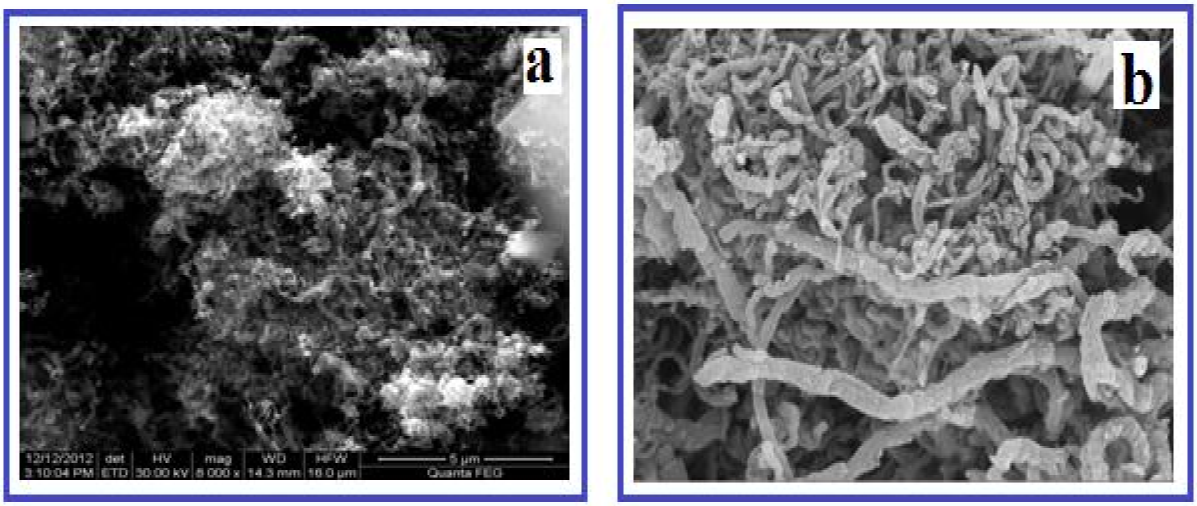

Fig. 2a & 2b: SEM images of CNT sample synthesized from experiments 1 & 2

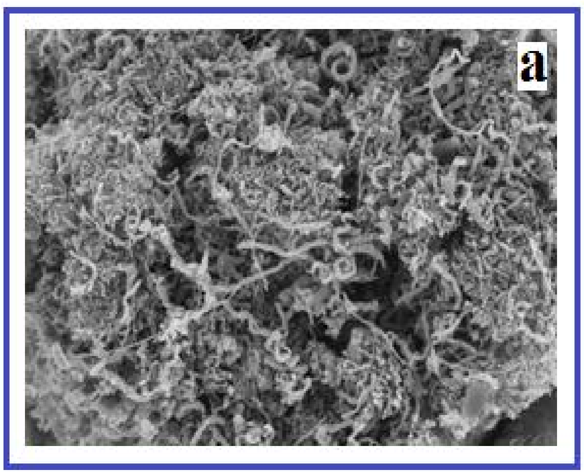

Fig. 3a: SEM image of sample fromExperiment 6

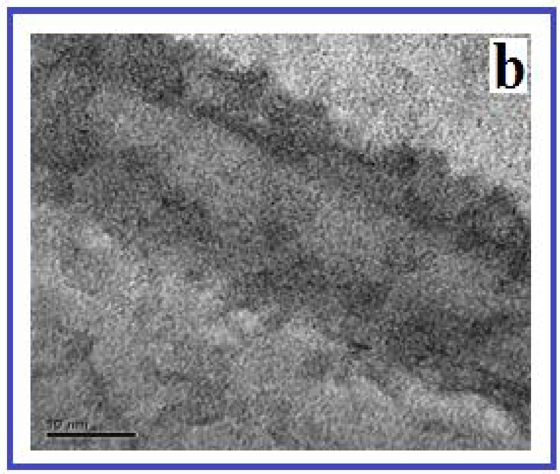

Fig. 3b: HRTEM image of sample from Experiment 16

Experiment 1 Fig. 2a presents a structure that looks like overlapping carbon crusts in which micro and nano particles are settled. This combination of growth parameters is not suitable for large scale synthesis of carbon nanotube. In experiment 2, carbon nanotubes diameter gradually increases due to the agglomeration of the catalyst particles in Fig. 2b. Likely the concurrent employment of a low feeding carbon source, low catalyst concentration and a rather low temperature is not a good environment for carbon nanotube growth. In experiment 3,4 9 and 12 there is no clear growth of carbon nanotubes and only some amorphous carbon layers can be observed because these temperatures are not sufficient to pyrolyse the carbon source and the catalyst activity is not enough. In experiment 5 the deposition of graphite like nanolayers was obtained.

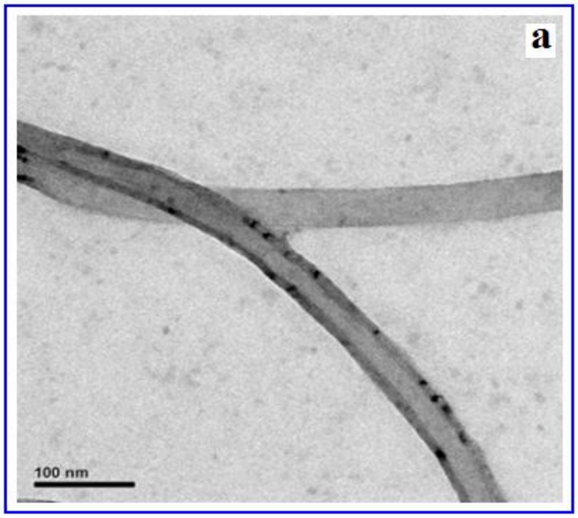

Fig. 4a: HRTEM image of as grown CNT

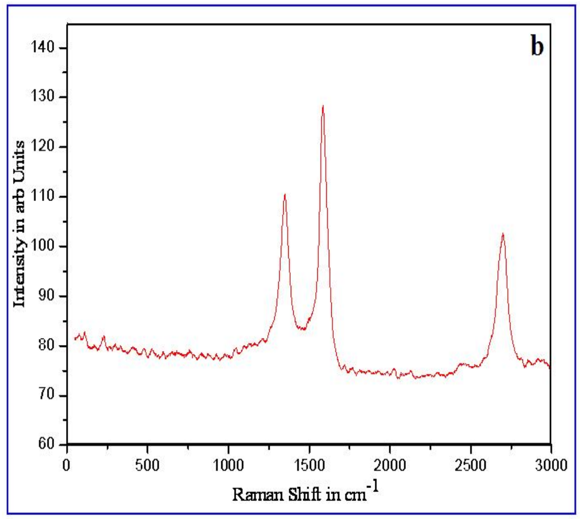

Fig. 4b: Raman spectra of as grown CNT

In experiment 6 Fig. 3a presents a typical massive growth of MWCNT on the catalyst surface. Catalyst surface is uniformly covered with web- like network of carbon nanotubes. Carbon nanotubes are nearly uniform in diameter with the diameter of about 23 nm. This indicates that the interaction between the support material and catalyst particle is very strong at this temperature. Therefore these settings allow growing thin nanotubes. These results are in good agreement with HRTEM images.

Representative HRTEM images are presented in Fig. 4a reveal that well graphitized multiwalled carbon nanotubes were formed. The quality of sample expt. 6 can be assessed by using Raman Spectrum shown in the Fig. 4b. I_D/I_G ratio of the sample was found to be 0.85. In experiment 7 and 16 in Fig. 3b layer of carabonaceous nanostructures of few micrometers thick are obtained. The nanostructures look like thick nanotubes covered by amorphous carbon.

The contour plot and three dimensional response surface obtained from second order polynomial equations are shown in the Fig. 5 & 6 respectively. The optimum values of the variable were obtained as the response is maximized using the RSM technique. The Best response range can be obtained by analyzing the response surface plots. The contour plots for the carbon nanotube yield was shown in the Fig. 5 indicates that the CNT yield as a function of various variables such as temperature, Flowrate of carbon source and catalyst ratio.

Fig. 6a depicts the 3D response surface relationship between temperature and the catalytic ratio on the yield of carbon nanotubes at constant flow rate of carbon source. It will be seen that at a given constant catalytic ratio, the yield of carbon nanotubes increased with increasing temperature up to a certain point, beyond which it is decreased. An increase in the temperature resulted in an increase in the yield of CNTs. At higher temperature, complete pyrolysis of carbon source takesplace so that the pyrolysed carbon atoms diffuse over catalyst particles and helps to initiate the growth of nanotubes. However, the yield of CNT decreased on further increasing in temperature as a result of the agglomeration of the catalyst particles.

The combined effect of flow rate of carbon source on the yield of MWCNT is shown in the Fig. 6b.

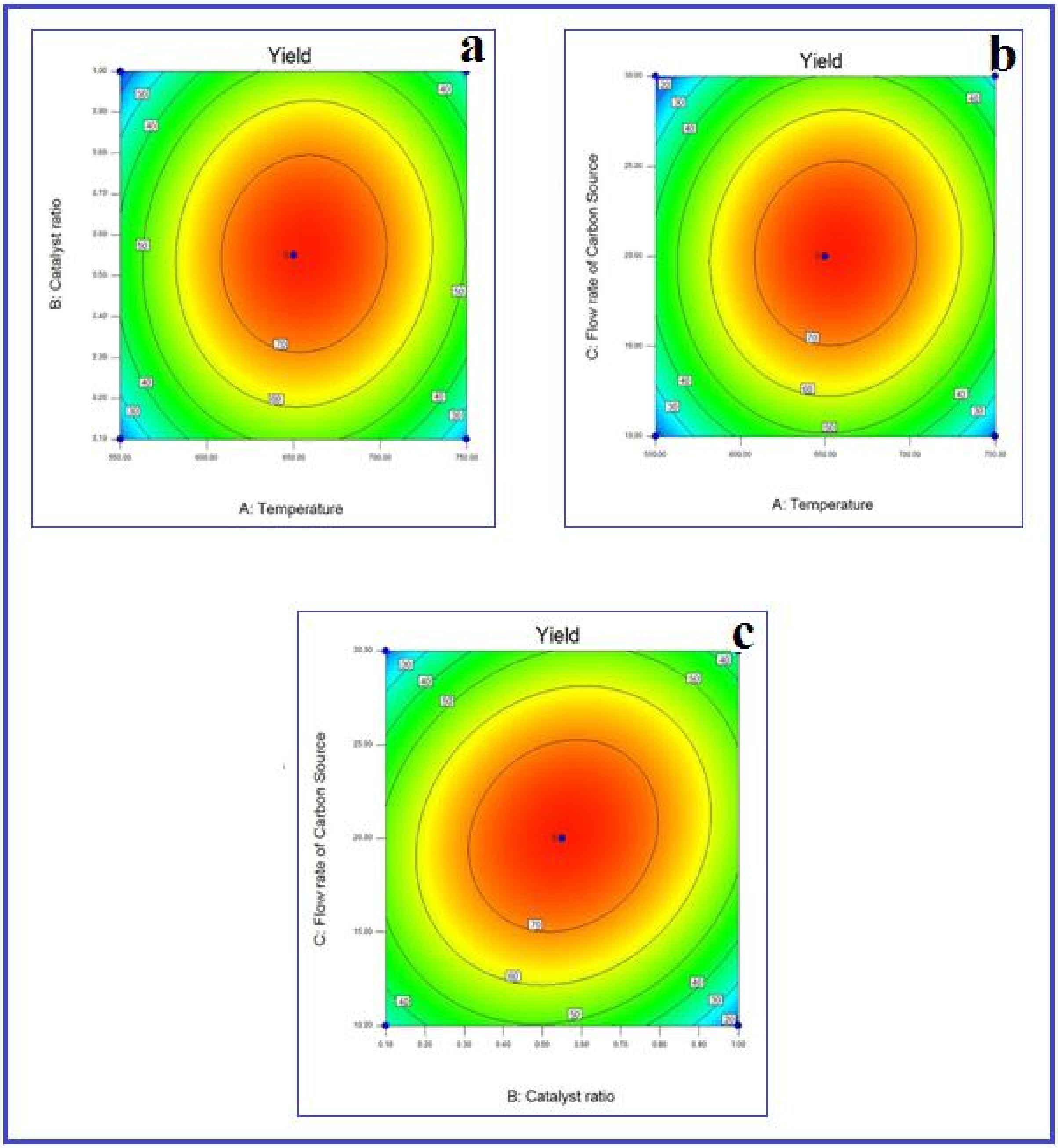

Fig. 5: Contour Plots of Yield (%) as the function of a) Temperature and Catalyst b) Temperature and Flow rate of carbon source c) Catalyst ratio and Flow rate of Carbon source

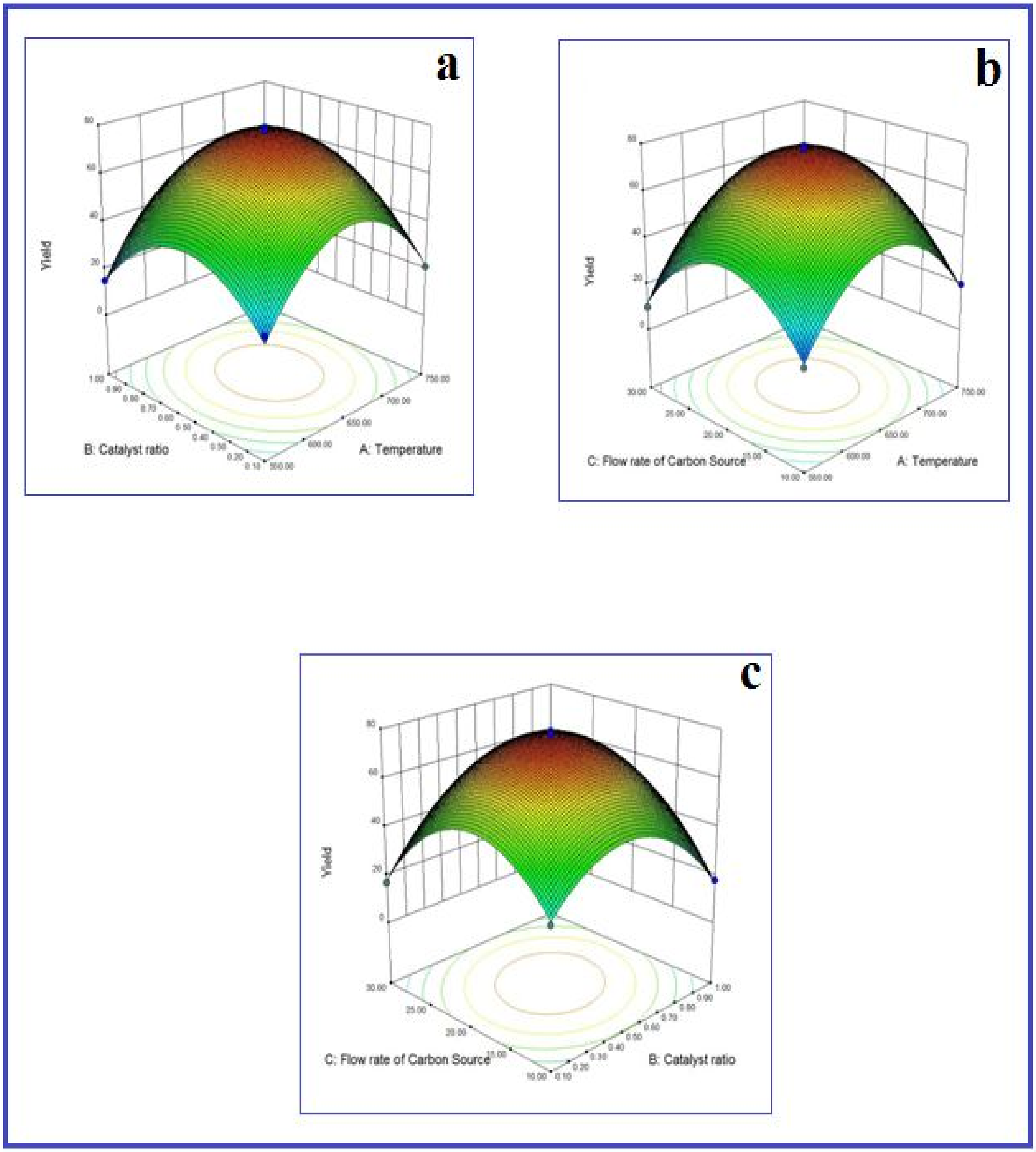

Fig. 6: Response surface plot of Yield (%) as the function of a) Temperature and Catalyst b) Temperature and Flow rate of carbon source c) Catalyst ratio and Flow rate of Carbon source

This implies that the yield of carbon nanotube increased with decreasing the flow rate of carbon source. This is due to high concentration of precursor is lead to the production of carbonaceous products as non-catalyzed decomposition is promoted.

The interactive influence of flow rate of carbon source and catalyst ratio on the yield of CNTs at constant temperature, could also be plotted as a response surface Fig. 6c . Catalyst is the main part for carbon nanotube nucleation: its size seems to be the determining factor for the formation of MWNTs or SWNTs and its diameter. The peculiarity of these transition metals to catalyze CNT formation is mostly linked to their catalytic activity for the decomposition of carbon compounds. Our preliminary experiments carried with Fe and Mo impregnated with silica gel shows that, the Mo catalyst grown CNTs having good graphitization compare to Fe catalyst grown CNTs. The variation in the concentration of the catalyst varies the quantity of CNTs growth.

The effect of temperature on the yield was in line and trend in the plot of the yield Vs catalyst ratio was similar to that depicted in Fig.6a over the experimental range examined. Optimization process was done for target value of 79 % of yield using response surface optimization process. The temperature, catalytic ratio and flow rate of carbon source had been found to be optimum conditions for maximum 77% of yield was obtained by using *Zea mays* Oil as the carbon source.

4. CONCLUSION

We reported on the successful application of the statistical design of experiments approach for the optimization of CVD synthesis of multiwalled carbon nanotubes by using *Zea mays* oil as the carbon source. The three key factors such as temperature, catalyst ratio and flow rate of carbon source affecting performance, were then optimized using Box- Behnken design. CNT with better physical and structural characteristics were obtained at a growth temperature of 656 °C, catalyst weight of 0.56 g and 20.2 ml of carbon source . This agrees with the HRTEM and Raman spectrum of as grown samples. Higher regression coefficient (R^2 = 0.9462) and higher adjusted regression coefficient Adj R^2 =0.9905) showed that a high significance of the model.

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